Towards an electroless deposition of gold on metallic substrates using ionic liquids as electrolytes

A.I. de Sá[1], S. Quaresma[2], S Eugénio[2], C.M. Rangel[1,2], and R.Vilar[2]

[1] Laboratório Nacional de Energia e Geologia, Paço do Lumiar 22,
Unidade de Pilhas de Combustível e Hidrogénio
1649-038 Lisboa, Portugal
[2] Departamento de Materiais, Instituto Superior Técnico, Universidade Técnica de Lisboa,
Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Abstract

Recent research has suggested a number of applications for gold in fuel cells and related hydrogen fuel processing, which include light weight corrosion resistance bipolar plates and the incorporation of gold as catalyst to provide improvements in electrode conductivity, among others. This paper reports on the electroless deposition of gold on copper substrates from a $HAuCl_4.3H_2O$ solution in 1-butyl-1-methylpyrrolidinium dicyanamide (BMP-DCA), in laboratory atmospheric conditions. The electrochemical behaviour of the plating solution was studied by potential sweep techniques. Results suggest that gold ions are reduced and deposited on copper without the aid of external polarization, probably by displacement deposition involving copper dissolution, since no other oxidation reaction was identified. Preliminary studies using SEM/EDX showed that compact gold thin films, deposited on copper substrates at 333 K, present a granular nanostructured morphology.

Keywords: *Electroless, Gold, Ionic Liquids, Electrodeposition, Thin films*

1 Introduction

There is an increasing interest in gold deposition for fuel cells applications, associated to the high corrosion /passivation resistance conferred to less noble substrates and to its catalytic properties. In the first case, gold coatings are being used in Polymer Electrolyte Membrane (PEM) bipolar plates to improve the performance of the materials currently tested, such as titanium or stainless steel [1, 2]. As a catalytic material, gold can have a significant role on purifying the hydrogen to be supplied to fuel cells as well as in the design of new catalyst [3].

Gold coatings are generally produced by electrodeposition using bath formulations that contain cyanides [4] and other toxic additives. Ionic liquids provide, in comparison, an alternative with reduced health and environmental impacts, with suitable properties to be used as electrolytes. In fact, they show low volatility, high chemical and thermal stability, and a conductivity that is, at least, equivalent to other organic solvents with added supporting electrolyte [5]. Under inert and dry conditions, the electrochemical window of some ionic liquids can extended up to 6 V, which allows depositing metals which ions are reduced outside the potential range for the chemical stability of water. Recently, ionic liquids have been examined as new electrolytes for electroplating different metals, including gold, as well as semiconductors materials [6].

The possibility of depositing gold in an electroless fashion, presents some advantages when compared with electroplated gold: no external power or elaborate equipment is necessary to produce thin uniform coatings, and it is more suitable to coat surfaces which include groves or other particular shapes such as PEM fuel cell bipolar plates.

In this paper, the 1-butyl-1-methylpyrrolidinium dicyanamide (BMP-DCA) ionic liquid is selected as a possible electrolyte for gold electroless deposition. The selection was based on the physical and chemical properties of the ionic liquid, including the viscosity, conductivity and complexing capability. The experiments were conducted in laboratory atmospheric conditions. In order to better understand the deposition process, voltammetry was performed on glass carbon and copper electrodes. Preliminary characterization of the gold coating, deposited on copper substrates,

was done by surface SEM observation and EDX analysis.

2 Experimental

The electrolyte for gold plating was prepared from analytical grade chemicals in the as-received condition, by dissolving $HAuCl_4.3H_2O$ (ACROS) in 1-butyl-1-methylpyrrolidinium dicyanamide (BMP -DCA, Merck) to the concentration of 0.020 M. The electrochemical experiments were performed using a 10 mL electrochemical cell with a three electrode configuration, exposed to laboratory atmosphere. The potential was measured against a platinum wire, considered a quasi-reference electrode (QRE). The counter electrode necessary for cyclic voltammetry was a platinum foil (area ~ 1 cm^2). Before the electrochemical experiments, the platinum electrode was activated by dipping in HNO_3 (65%) during one minute. Copper electrodes were polished, firstly with carbon paper (1000 mesh) and then with diamond paste of 6 and 3 µm. Finally the specimens were activated by dipping in a H_2SO_4 solution (1:10). The electrochemical data were acquired with a potentiostat (EG&G PAR, model 173) using "Corrware" software. A Philips Scanning Electron Microscope, Model XL 30 FEG, equipped with energy dispersive X-ray spectroscopy (EDX) was used.

3 Results and Discussion

3.1 Solvent selection

Ionic liquids based on imidazolium ion (Fig. 1), such as 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF_4) or basic mixtures of 1-butyl-3-methylimidazolium chloride (BMI-Cl) plus aluminium chloride, have already been studied as electrolytes for gold electrodeposition [7, 8]. On the other hand, 1-butyl-1-methylpyrrolidinium dycianamide (BMP-DCA) has been tested as a potential electrolyte mainly due to its strong complexing capability, based on the Lewis character of the DCA anion, which induces high solubility of many metal chlorides [9]. In fact, results obtained with this ionic liquid, after addition of $HAuCl_4.3H_2O$, have shown good results for gold electrodeposition. Table 1 compares physical properties such as the conductivity, viscosity and density for the mentioned ionic liquids or mixtures at room temperature; the lower the viscosity the more efficient the mass transport, essential in electrodeposition processes. In view of the mentioned properties, BMP-DCA was selected, in this work, as potential solvent for the electroless deposition of gold. The fact that BMP-DCA is very hygroscopic was seen as an advantage since the uptake of water by the ionic liquid contributes to an increase in the conductivity of the electrolyte.

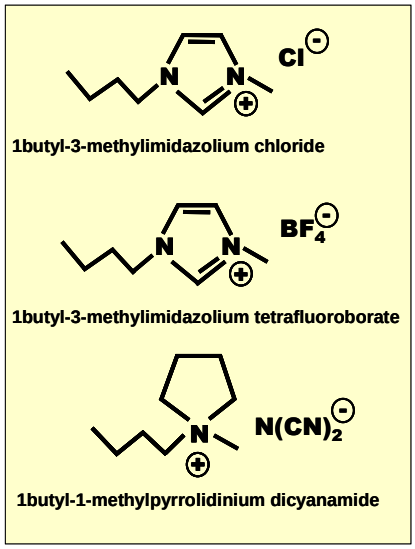

Fig. 1 Common ionic liquids based on imidazolium and pyrrolidinium cations.

Table 1 Physical properties of some ionic liquids and mixtures already used for gold electrodeposition at room temperature.

Ionic Liquid/ Property	BMI-Cl + $AlCl_3$ (50%)	BMI-BF_4	BMP-DCA
Conductivity (mS cm^{-1})	10.0[10] (298 K)	3.5[6] (298 K)	11.7* (298 K)
Viscosity (cP)	27[11] (n.a)	180[6] (298 K)	45.3[6] (298 K)
Density (g cm^{-3})	1.29[10] (298 K)	1.21[6] (298 K)	0.95[6] (298 K)

* in this work (without any drying procedure).
n.a = not available

3.2 Potential sweep techniques

The polarization curves obtained for copper in pure BMP-DCA and BMP-DCA + 0.020 M $HAuCl_4.3H_2O$, in laboratory air conditions, at a scan rate of 100 mVs^{-1} and 298 K, are presented in Figure 2. The most significant feature is the high

values of the current density on the anodic side of both curves which is associated to copper dissolution.

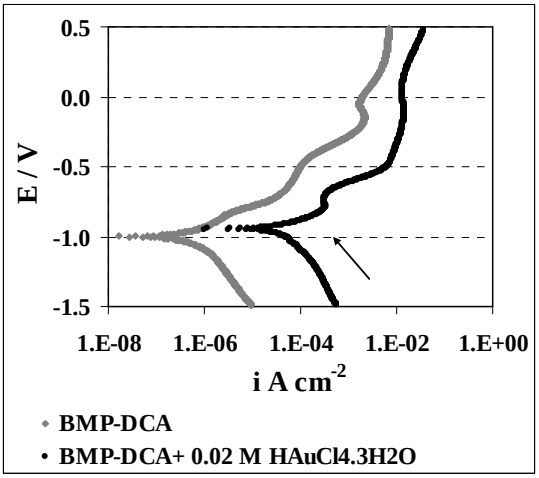

Fig. 2 Polarization curves obtained for copper in pure BMP-DCA and BMP-DCA + 0.020 M $HAuCl_4.3H_2O$ solution at 298 K.

No features directly associated to the reduction of gold ions were identified. However, the cyclic voltammograms carried out in the same experimental conditions on a glassy carbon, electrode, which is a more inert surface, at 298 and 333 K (see Fig. 3), showed two cathodic peaks associated to the gold reduction processes: Au(III) to Au(I) and Au(I) to Au(0).

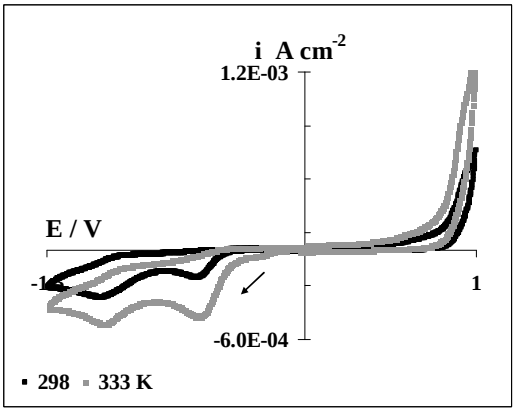

Fig. 3 Cyclic voltammograms obtained for glassy carbon BMP-DCA and BMP-DCA + 0.020 M $HAuCl_4.3H_2O$ solution at 298 and 333 K.

The polarization curves carried out in the deposition solution at 298 K and in the pure ionic liquid show that copper is easily dissolved since there is a significant increase of the current density above the open circuit potential. So, it seems likely that copper oxidation will be the complementary oxidation for the reduction of gold ions. These preliminary results suggest that the redox process associated to the gold deposition is a displacement process of copper by gold:

$$2Au^{3+} + 6e \rightarrow Au \qquad (1)$$

$$3Cu \rightarrow 3Cu^{2+} + 6e \qquad (2)$$

However, due to the complex nature of the solvent, associated to the presence of a certain amount of water and chloride ions, secondary reactions may contribute to the overall deposition process. This is the subject of on-going research.

3.3 Gold deposition

Thin films of gold were obtained, in laboratory atmospheric conditions, by exposure of copper substrates to a solution of 0.02 M $HAuCl_4.3H_2O$ in BPM-DCA, at 333 K during 1500 s, at the open circuit potential (Eoc). Immediately after immersion, the registered Eoc value was -0.900 V following an irregular increase with exposure time to a slightly more anodic potential (-0.854 V), as shown in figure 4.

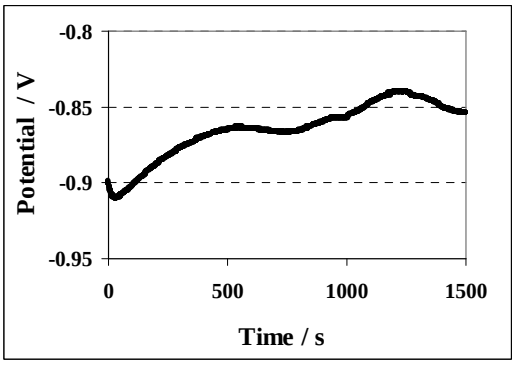

Fig. 4 Potential versus time for the gold deposition on copper substrate (BMP-DCA + 0.020 M $HAuCl_4.3H_2O$ solution, 333 K, 1500 s).

3.4 Film Morphology

The copper surface is found, after immersion in BMP-DCA+ 0.020 M $HAuCl_4.3H_2O$ solution and without the aid of external polarization, to be covered by a golden brown film. SEM observation is presented in figure 5a. EDS analysis confirms the presence of gold and copper (Fig. 5b): no other

elements such as oxygen, chlorine or nitrogen were detected. The films are characterized by a granular nanostructured morphology constituted by aggregates with a wide distribution in diameter (Fig. 5c).

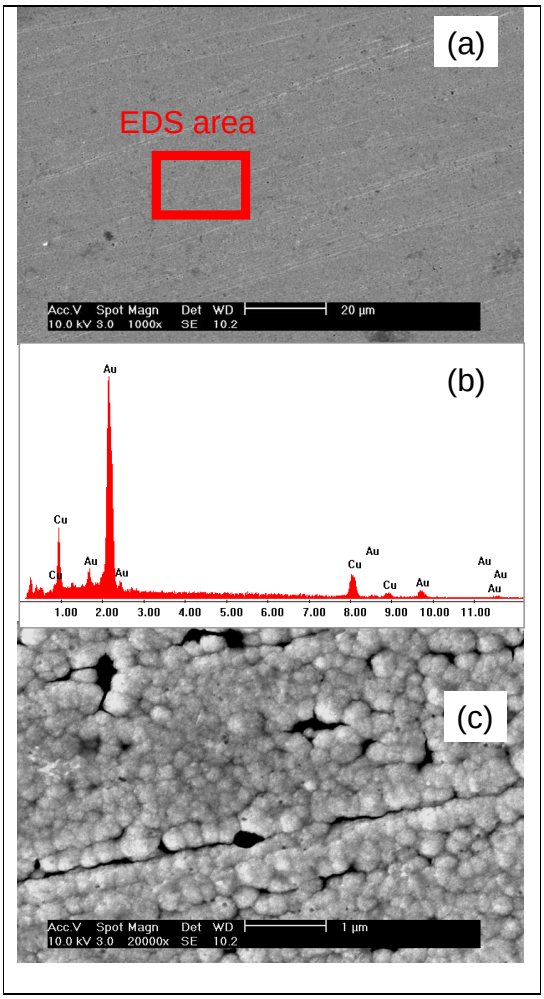

Fig. 5 Scanning electron micrographs after gold deposition on a copper substrate (0.020 M $HAuCl_4.3H_2O$, 333 K, 1500 s): low magnification (a) with the correspondent EDS spectrum (b) and high magnification (c).

4 Concluding remarks

- The BMP-DCA ionic liquid is a suitable electrolyte for gold deposition without the aid of an external polarization source.
- Thin films of gold are obtainable on copper substrates, using solutions of $HAuCl_4.3H_2O$ in BMP-DCA at 333 K. The films are formed by granular aggregates of nanoparticles.
- Gold thin films are obtainable under laboratory atmospheric condition, avoiding the need for the use of equipment to keep low levels of moisture and oxygen.

Acknowledgements

This work was financially supported by the Portuguese Foundation for Science and Technology (FCT) under the Project PTDC/CTM/68847/2006.

References

[1] S-H Wang, J Peng, W-B Lui and J-S Zhang, *Performance of the gold-plated titanium bipolar plates for the light weight PEM fuel cells*. Journal of Power Sources 162 (2006):486-492.
[2] J. Wind, R. Späh, W. Kaiser and G. Böhm, *Metallic bipolar plates for PEM fuel cells*, Journal of Power Sources 105 (2002):256-260.
[3] D. Cameron, R. Holliday and D. Thompson, *Gold's future in fuel cells*, Journal of Power Sources 118 (2003):298-303.
[4] H.O Ali. H.O. and I.R.A. Christie, *A Review of Electroless gold deposition processes*, Gold Bull., 17(1984) 118.
[5] M. Galinski, A. Lewandowski, and I. Stepniak, *Ionic liquids as electrolytes*. Electrochim. Acta, 51 (2006) 5567-5580.
[6] S.Z.E Abedin, and F. Endres, *Electro-deposition of Metals and Semiconductors in Air and Water-Stable Ionic Liquids*. Chemphyschem, 7 (2006). 58-61.
[7] X-H Xu, and C.L. Hussey, *The Electrochem. of Gold at Glassy Carbon in the Basic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Molten Salt*, J. Electrochem. Soc., 139 (1992) 3103-3108.
[8] T. Oyama,, T. Okajima, and T. Ohsaka, *Electrodeposition of Gold at Glassy Carbon Electrodes in Room-Temperature Ionic Liquids*, J. Electrochem. Soc., 154 (2007). D322-D327.
[9] M-J Deng, P-Y Chen, T-I Leong, I-W Sun, J-K chang and W-T Tsai, *Dicyanamide anion based ionic liquids for Electrodeposition of Metals*, Electrochem. Commun., 10 (2008) 213-216.
[10] J. Vaughan, J. Tu and D. Dreisinger, *Ionic Liquid Electro-deposition of Reactive Metals*, Sohn Intern. Symposium on Advanced Processing of Metals and materials, San Diego California, 27-31 August, 2006, California.
[11] R.G. Reddy, *Editorial*, Journal of Phase Equilibria and Diffusion, 27(2006) 210-211.